On the Structure of 2-Mercaptotropones

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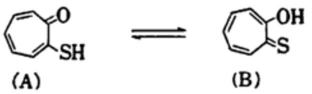
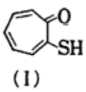
2-Mercaptotropone (I) was synthesized in 1953 by Nozoe and his collaborators[1,2]. It comes as reddish orange crystals of m. p. 55°C and the compound was assumed to be present in two tautomeric forms, A and B. Alkylation



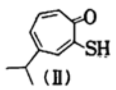
(A) (B)

and acylation of I afford only sulfur-substituted derivatives, while reaction with hydrazine gives 2-hydrazinotropone. Bromine easily effects an oxidation to 2, 2′-ditroponyl disulfide. These facts suggest a structure A of this compound and this was named 2-mercaptotropone. But further examination on its physicochemical properties as well as those of its homologs suggested that this should rather be a 2-hydroxyl derivative of tropothione, structure B, and details of this work are described herein.

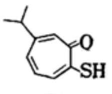
Physical measurements were carried out with 4-isopropyl-2-mercaptotropone (II), 6-isopropyl-2-mercaptotropone (III), 2-methylthiotropone (IV), 4-isopropyl-2-methylthiotropone (V), and 6-isopropyl-2-methylthiotropone (VI)[3], besides the 2-mercaptotropone (I).



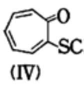
(I)



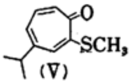
(II)



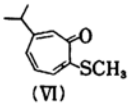
(III)



(IV)



(V)



(VI)

Ultraviolet Absorption Spectra[4].—The ultraviolet absorption spectra of I, II and III are indicated in Fig. 1 and those of IV, V and VI in Fig. 2. As will be seen from these, the spectral curve of 2-mercaptotropones in Fig. 1 shows a fair shift to the longer wavelength side than that of 2-methylthiotropones in Fig. 2, indicating that there is an essential difference in the structure of these two kinds of compounds. This relationship is the same as that between 2-thiopyridone and its *S*-methyl derivative[5], and if the B type of the structure is assigned to 2-mercaptotropones, the difference in ultraviolet absorptions could be explained as a bathochromic shift due to the C=S group.

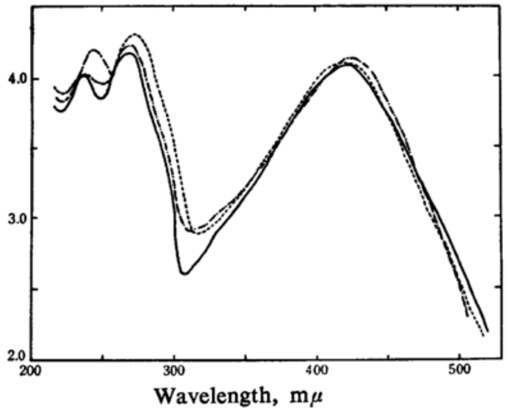


Fig. 1. Ultraviolet absorption spectra in cyclohexane.
——— I - - - - - - II —·—· III

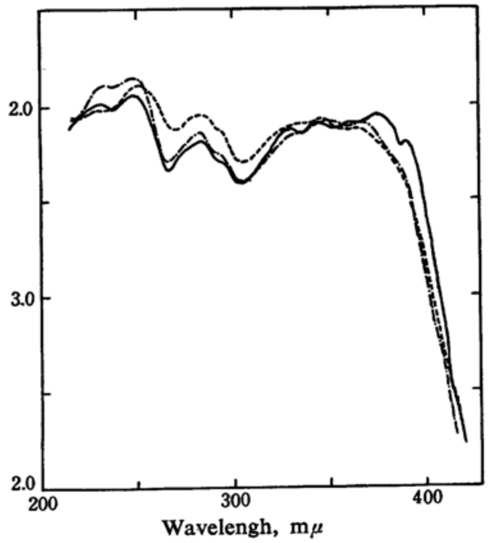


Fig. 2. Ultraviolet absorption spectra in cyclohexane.
——— IV - - - - - - V —·—· VI

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[1] T. Nozoe, M. Sato and K. Matsui, *Proc. Japan Acad.*, **29**, 22 (1953).

[2] Idem, *Sci. Repts. Tohoku Univ.*, *I*, **37**, 211 (1953).

[3] K. Matsui, This Bulletin, **33**, 1448 (1960).

[4] Measured by a Beckman Model DU spectrophotometer.

[5] A. Albert and B. Barlin, "Current Trends in Heterocyclic Chemistry", Butterworths Scientific Publications, London (1958), p. 51.

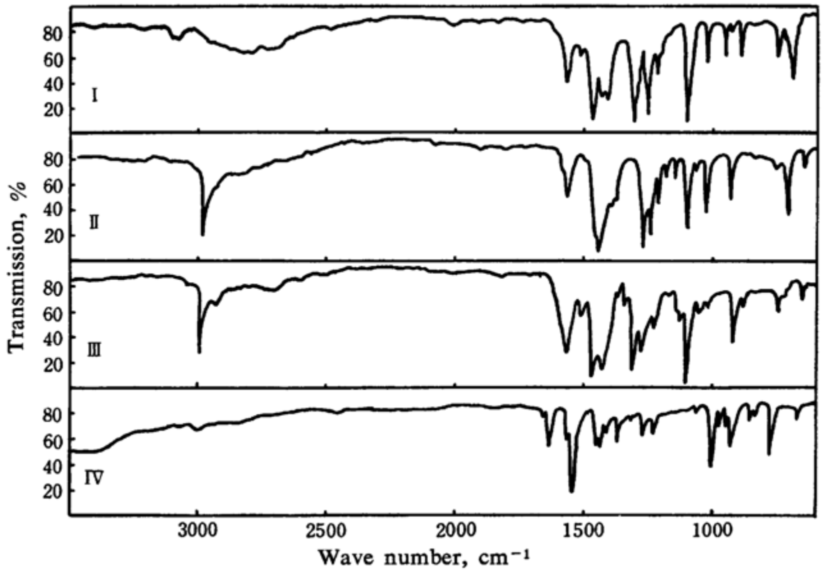

Fig. 3. Infrared absorption spectra.

I in 0.5% CCl$_4$ soln. II in 0.5% CCl$_4$ soln.
III in 0.5% CCl$_4$ soln. IV in KBr-pellet

Infrared Absorption Spectra[2,6]. — Infrared absorption spectra of I, II, III and IV are shown in Fig. 3. The absoprtion of IV in the double-bond region is similar to those observed in tropone, 2-methoxytropone, and 2-halotropone[7], but the spectra of I, II and III are quite different from those seen in tropones and tropolones in general. Furthermore, examination of the spectra of I in the 3000 cm^{-1} region indicates the presence of a broad and weak absorption in the region of 3000～2600 cm^{-1}. It is rather appropriate to consider that I takes the structure B and the ν_{OH} absorption has been shifted to lower wave-numbers by chelation, than a shift of ν_{SH} absorption to higher wave-numbers side from the usual absorption at 2600～2550 cm^{-1}.

The absence of a strong absorption assignable to the C=O group in a higher wave-numbers side than 1500 cm^{-1} in the double-bond region also agrees with the structure B and considering Mecke's law[8] the absorption at 1100 cm^{-1} is assumed to correspond to $\nu_{C=S}$.

The same thing may be said of II and III, and 2-mercaptotropones are therefore assumed to take the B of the type structure from infrared absorption spectral examinations.

Nuclear Magnetic Resonance Spectra[9].—

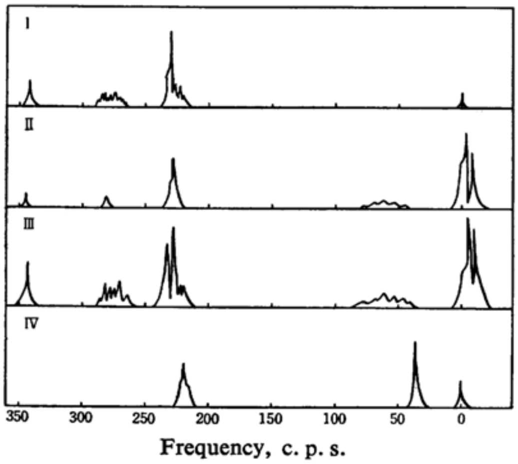

Fig. 4. NMR spectra of I, II, III and IV.

The NMR spectra of I, II, III and IV were measured in carbon tetrachloride solution at 40 Mc./sec. at room temperature, with cyclohexane as the internal reference. The results are indicated in Fig. 4. It should be noted here that in I, II and III, the resonance line of the ring proton appears as two signals, at 280 and 230 c. p. s. Since the ring proton appears as one signal at ca. 240 c. p. s. in tropone and tropolone[10], the small signal at 280 c. p. s. in the considerably lower magnetic field side should be assigned to the ring proton

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[6] Measured by a Perkin-Elmer Model 21 double beam spectrophotometer.

[7] S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts. Reseach Inst. Tohoku Univ.*, A-8, 264 (1956).

[8] R. Mecke, R. Mecke and A. Lüttringhaus, *Chem. Ber.*, **90**, 975 (1957).

[9] Measured by a Varian V 4300 B spectrometer.

[10] D. Ginsberg, "Chemistry of Non-benzenoid Aromatic Compounds", Interscience Publishers, New York (1959), p. 380.

next to sulfur group. Further, the fact that this is absent in IV suggests that, I, II and III take the B type of the structure, and the signal of proton attached to the carbon next to the C=S group appears in the lower magnetic field side because is it in a different magnetic surrounding from other protons.

The resonance line at ca. 340 c. p. s. in I, II, and III may be assignable to SH group, but the OH line in tropolone appears at ca. 280 c. p. s.[10] This is in reverse of the general observation that the resonance line of SH compounds appears in a higher magnetic field than the corresponding OH compounds[11,12]. This fact also denies the A type of the structure.

pK_a value.—The fact that pK_a value of I (5.89)[13] is smaller than that of tropolone (6.92)[14], is in agreement with the general observation that thiophenols show smaller pK_a value than the corresponding phenols. The difference of I and tropolone is, however, only 1 pK_a unit, and this rather small difference compared with that, ca. 3 pK_a unit[15,16], between thiophenols and phenols might be explained by the assignment of the structure B rather than A to I as follows.

2-Thiopyridones[17] show smaller pK_a values than the corresponding 2-pyridones[18] by ca. 2 pK_a unit, which is presumably due to the difference in inductive and mesomeric effect between the C=S and the C=O group. Similarly, it might be expected that in the case of I, structure B, and the tropolone, the C=S group in I should activate the OH group, more than the C=O group in tropolone does. But spacious and electron-rich sulfur atom induced by these electronic effects of the C=S group, conversely tend to control the liberation of proton in the OH group located close by*, more than does the oxygen atom in tropolone.

As a result of these opposing effects of the C=S group in I, the small pK_a difference between I and tropolone is understandable without inconsistency.

Solubility. — Mercaptans in general are practically insoluble in water, but the solubility of I in water is 0.846 g./l.[13] Such a large degree of solubility also supports the structure B.

The results of the foregoing ultraviolet, infrared, and NMR spectral measurements, pK_a value, and solubility, all indicate the appropriateness of the B type of the structure for 2-mercaptotropones. It has therefore been clarified that, although the compounds behave as A type of the structure during various reactions, they take the B type of the structure in a static state.

Consequently, the conventional structure A for 2-mercaptotropone (I) should be corrected and the structure B, i. e. 2-hydroxytropothione, is forwarded.

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[11] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, 77, 3977 (1955).

[12] L. H. Meyer, A. Saika and H. S. Gutowsky, ibid., 75, 4567 (1953).

[13] N. Yui, *Sci. Repts. Tohoku Univ.*, *I*, 40, 114 (1956).

[14] Idem., ibid., 40, 50 (1956).

[15] G. Schwarzenbach and H. Egli, *Helv. Chim. Acta*, 17, 1176 (1934).

[16] W. H. Fletcher, *J. Am. Chem. Soc.*, 75, 3784 (1953).

[17] R. A. Jones and A. R. Katritzky, *J. Chem. Soc.*, 1958, 3610.

[18] A. Albert and J. N. Phillips, ibid., 1956, 1294.

* It should be noted here that tropone and tropolone derivatives with the SH group are extremely unstable and undergo dehydrogenative condensation to yield disulfides, unless the SH group is situated at the carbon next to the C=O group and a hydrogen bond between these groups is formed[2].